Supporting Material on
Competition for graphene: graphynes with directional-dependent Dirac cones

Daniel Malko, Christian Neiss, Francesc Viñes, and Andreas Görling
Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany
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COMPUTATIONAL DETAILS

Periodic slab calculations based on the Kohn-Sham formalism of DFT were carried out using the VASP program package [1]. The exchange-correlation functional according to Perdew, Burke, and Ernzerhof [2] (PBE) was employed. The projector augmented wave method [3] has been used to represent the atomic cores. A cutoff of 415 eV was chosen for the plane wave basis set leading to a convergence of total energies below 0.001 eV as corroborated by calculations with higher cutoffs. The convergence criterion of the self-consistency process was set to 10^{-7} eV. A Monkhorst pack k-point grid with 17×17, or 31×31 k-points in the xy-plane and one k-point in the z-direction was chosen for α-graphyne and β-graphyne, or 6,6,12-graphyne, respectively. Test calculations showed that results are fully converged with respect to k-points. Geometries were determined by optimizing both the unit cell vectors in the xy-plane and the positions of the atoms within the unit cell. The length of the unit cell in z-direction with 15 Å was chosen large enough that no interaction between different graphyne layers occurs. During the geometry optimization forces acting on the atoms were required to become smaller than $10^{-3}\,\mathrm{eV\,Å^{-1}}$. The obtained geometries were checked to be minima of the potential energy surface by numerically calculating second derivatives of the energy by shifting each atom in each direction by 0.05 Å. During the geometry optimization a Methfessel-Paxton smearing of order one with 10^{-3} eV half width was employed. DOS were calculated using the tetrahedron method in conjunction with large k-point grids in the xy-plane. Repeating calculations with an exchange-correlation functional within the local density approximation showed that the results presented here do not depend on the choice of the approximation for the exchange-correlation functional. The robustness of the band structures was tested by carrying out geometry optimizations in slightly distorted unit cells. Stretching or compressing the rectangular unit cell of 6,6,12-graphyne, e.g., resulted in only minor changes of the band structure, both Dirac points of 6,6,12-graphyne remained intact.

[1] G. Kresse and J. Furthmüller, Phys. Rev. B. **54**, 11169 (1996).
[2] J. P. Perdew, L. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[3] P.E. Blöchl, Phys. Rev. B, **50**, 17953 (1994).

SUPPLEMENTAL FIGURES

In the supplementary Fig. 1-4 the two orbitals (one-electron wave functions) at the Dirac points of graphene and all investigated graphynes are shown. In supplementary Fig. 5 a two-dimensional plot of the band structure of 6,6,12 graphyne in the irreducible part of the Brillouin zone is displayed.

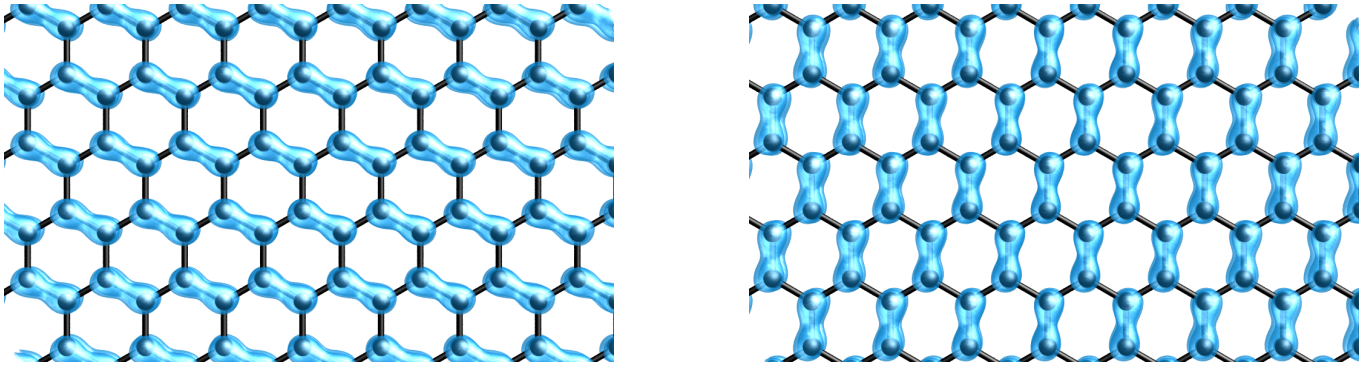

FIG. 1. Charge density-plots of the two orbitals (one-electron wave functions) at the Dirac point of graphene for a contour value of $0.3\,\text{Å}^{-3}$.

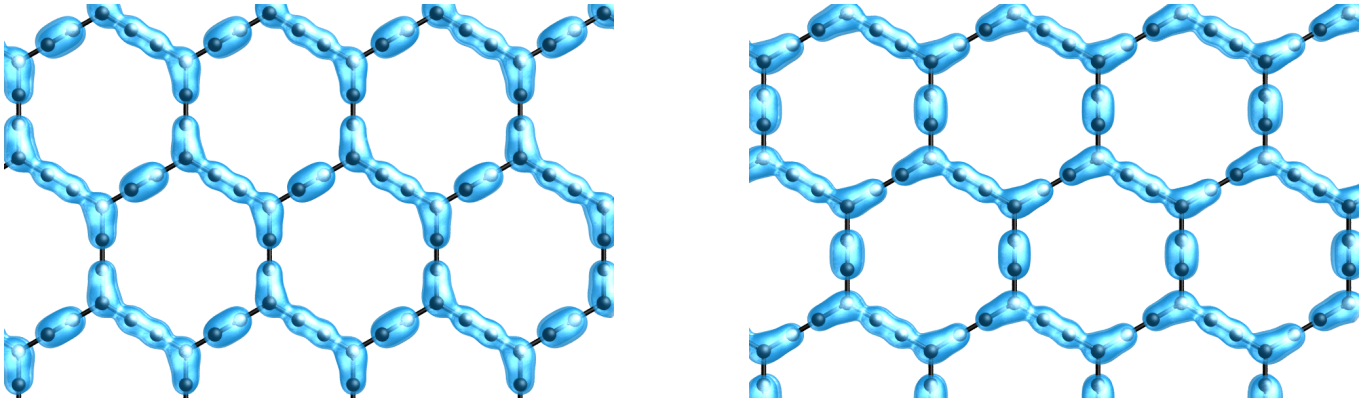

FIG. 2. Charge density-plots of the two orbitals (one-electron wave functions) at the Dirac point of α-graphyne for a contour value of $0.04\,\text{Å}^{-3}$.

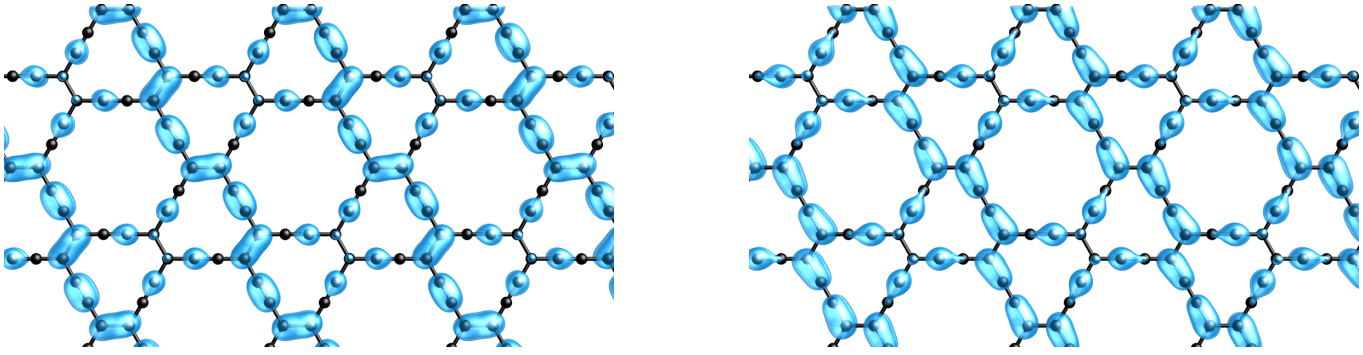

FIG. 3. Charge density-plots of the two orbitals (one-electron wave functions) at the Dirac point of β-graphyne for a contour value of $0.02\,\text{Å}^{-3}$.

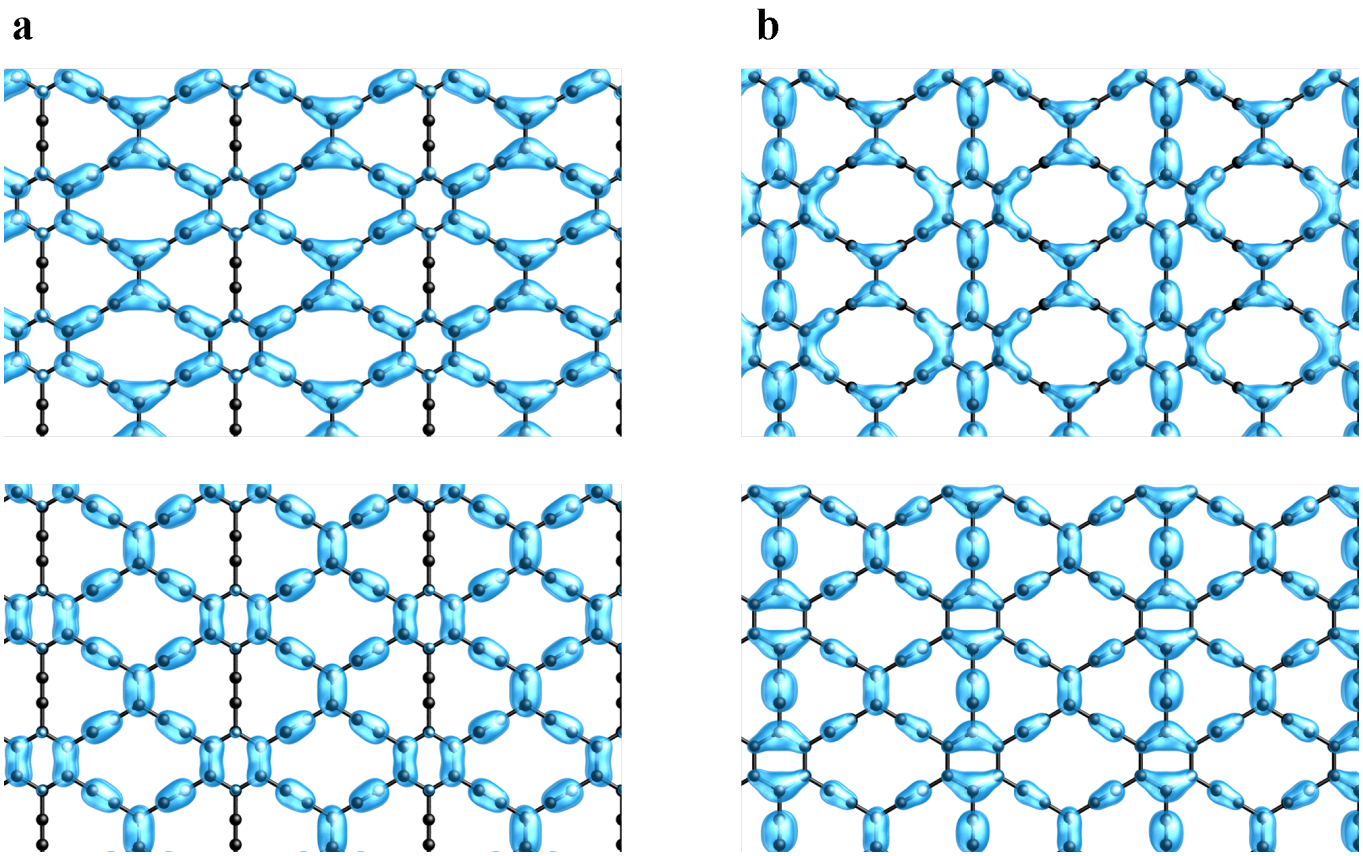

FIG. 4. Charge density-plots of states at the Dirac points of 6,6,12-graphyne. **a**, Charge density of orbitals (one-electron wave functions) at the Dirac point I. **b**, Charge density of orbitals (one-electron wave functions) at the Dirac point II. All charge densities are plotted for a contour value of 0.02 $Å^{-3}$.

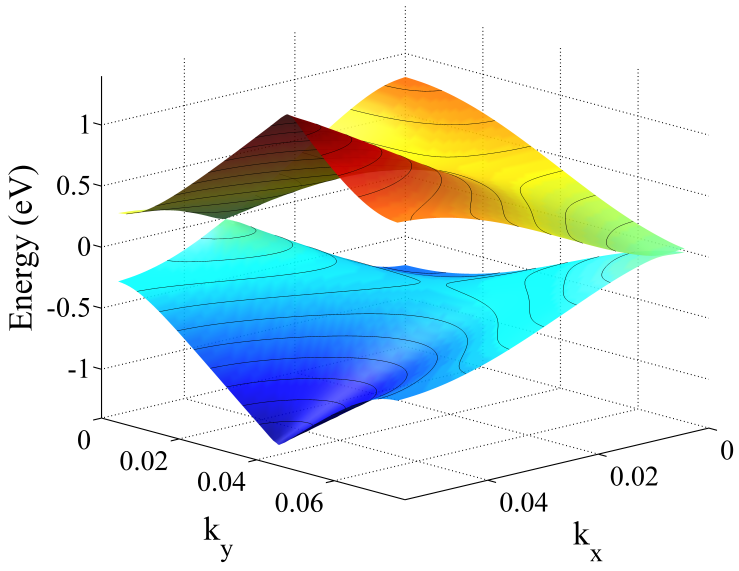

FIG. 5. Two-dimensional plot of the band structure of 6,6,12-graphyne in the irreducible part of the Brillouin zone.